Application Note: PI2044.0207

SOLA II — Trace Sulfur Analysis in the Production of Biofuels

Key Words

- Biodiesel/Bioethanol
- Environmental Regulations
- Total Sulfur Analyses
- 24 hours a day, 7 days a week
- Total Sulfur Concentration
- Field Sulfur Analyzer
- ASTM D5453
- ISO 20846

Introduction

Biofuels (i.e., bioethanol, biodiesel) are rapidly transitioning from an alternative form of energy to a viable, long term solution to reduce demand on rapidly depleting fossil fuel supplies. Based on a target set by the U.S. government, it is projected that 30% of the national fuel supply will be biofuel by the end of 2030. The European Union projects 2% of its countries' fuel supply will be biofuel by the end of 2007, increasing to 6% in 2010 and 20% by 2020. This anticipated demand, along with sizable investments, are fueling the growth of process plants globally, with the number of U.S. plants expected to double by 2009. Fuel producers that are currently blending traditional fuels with the new "greener" specifications are driving the current demand for increased supply.

The genesis of biofuels is root or seed crops. Because they are inherently "clean" by nature, the use of biofuels results in large scale reductions of soot, particulates, aromatics, and sulfur. The high lubricity of biofuels enables the achievement of low levels of fuel blend sulfur without compromising fuel performance.

Currently, biofuels are blended with traditional motor fuels to produce blended specifications for use in unmodified engines. These blends include:

- E10 (10% bioethanol + 90% gasoline) which can be used in all gasoline fueled vehicles.
- E85 (85% bioethanol + 15% gasoline) which can be used in flex fuel vehicles only.
- B5 (5% biodiesel + 95% gasoil) which is considered to be an additive blend. This 5% biodiesel blend meets ASTM specifications for Gasoil #2 and is known to clean injectors, boost cetane and improve lubricity.
- B20 (20% biodiesel + 80% gasoil) which provides the best emission reduction at the lowest cost.
- B99 (99.9% biodiesel + 1% gasoil) which provides the best emission reduction.

To ensure regulatory compliance, there are quality standards in place for biofuel production, including ASTM 6751 and EN 14214. Bioethanol is also addressed by ASTM 4806. The standard test procedure for sulfur analysis in biofuels is ASTM D5453.

Why Test for Sulfur in Biofuels?

With a negligible amount of sulfur present in biofuels, the question most asked is: Why test for sulfur? There is an expectation that biofuels should not be a sulfur contributor to the final fuel blend. This is, in itself, a reason for biofuel producers to demonstrate the "sulfur free" nature of their products. There are two areas where contamination can occur. Processing catalysts that contain sulfur can carryover from the manufacturing process into the biofuel product. Additionally, sulfur in the feedstocks can, upon reaction, end up in the biofuel product.

Biodiesel (or Fatty Acid Methyl Ester to be precise) is manufactured by the transesterifiation of vegetable-based oils and fats. To neutralize the reaction process and "fix" the end point of the

figure 1 — Therm Scientific SOLA II

reaction, acids such as phosphoric or sulfuric are added. Trace amounts of the liquid catalyst used in the process can break through into the finished product along with residual proteins (i.e., amino acids). Residual acid, catalyst and protein can contribute to a sulfur presence in the finished product.

During the bioethanol production process, the sulfur containing biomass feed is hydrolyzed with acid. The hydrolysis of sulfur containing plant proteins can cause the formation of sulfur compounds in the biofuel product. Catalyst carryover can also lead to higher than acceptable sulfur levels in the finished product.

In short, the manufacturing process in each case can lead to variations in finished product quality and sulfur content. With specifications established for "trace" sulfur content at 10 parts per million (ppm) or less, minor contamination can quickly move a product out of specification.

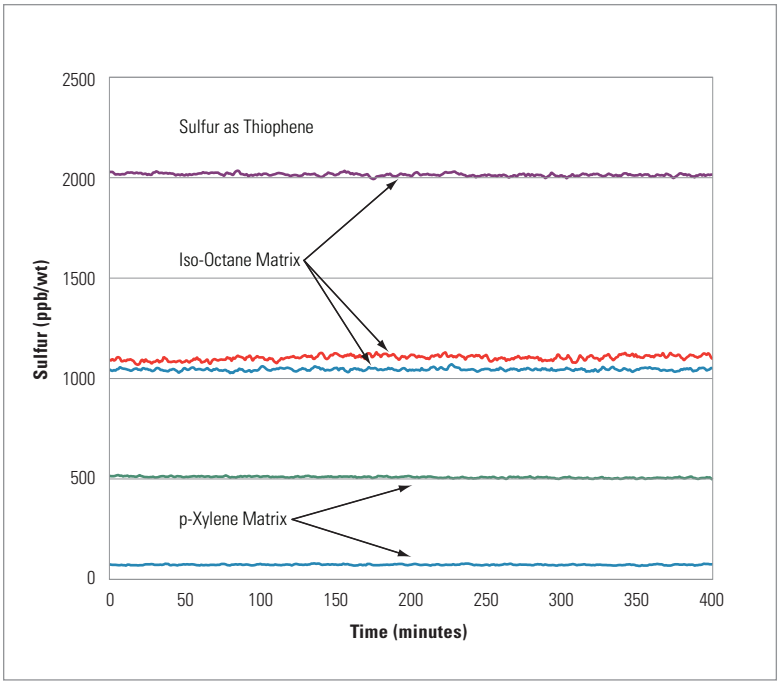

figure 2 – SOLA II trace stability comparison

Implementation of Sulfur Analysis

The size and nature of a company's production facilities will dictate how the company implements procedures to control and monitor sulfur in finished biofuels. Plants producing smaller batches may opt for offline laboratory testing as a sufficient means to establish product quality prior to shipping. However, larger companies with continuous plant operations often times leave themselves exposed by relying on laboratory sampling methods.

There is a significant amount of time involved in taking a sample offline, sending it to the laboratory, scheduling, running analysis and reporting the results. This time lag can lead to product being loaded into tankers, shipped and even delivered prior to the results being known. The only way to prevent this situation is to quarantine the material in expensive storage facilities until the quality is established in the laboratory and reported back to operations. Furthermore, laboratory analysis is only available when there is laboratory staff available.

For continuous and RFT/JIT (right first time/just in time) manufacturing processes, continuous online process analysis and control is the only viable option. An online analyzer can readily provide 24/7 sulfur concentration information, which allows operators to isolate rundown streams or divert product identified as out of specification in a timely, economical manner. In some cases, this product can be blended or reworked with good quality product to avoid operating losses.

The Thermo Scientific SOLA II has earned a reputation as the leading online, continuous sulfur analyzer for use during hydrocarbon fuel production. Its success with online fuel blending applications and trace sulfur analysis for catalytic processes indicates the SOLA II is an effective, adaptable analyzer. The performance of the SOLA II on trace sulfur levels, along with its reliability and response time, make it well positioned to continuously monitor sulfur levels during biofuel production.

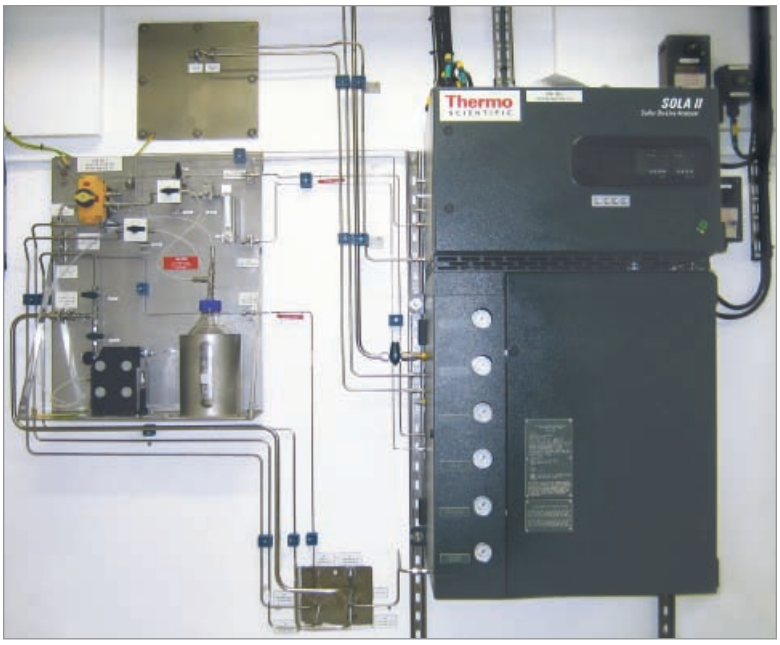

figure 3 – SOLA II typical field installation

SOLA II Principle of Operation

The SOLA II employs pulsed ultraviolet spectrometry (PUVF) for determination of total sulfur. To determine the total sulfur content of hydrocarbon samples by PUVF, all organically bound sulfur is converted to sulfur dioxide (SO_2) by sample combustion. Irradiation of SO_2 with a specific wavelength of ultraviolet light forms an electronically excited form of SO_2. The electronically excited SO_2 relaxes to its ground state by the emission of light or fluorescence. The intensity of the emitted light is directly proportional to the SO_2 concentration and thus the biofuel's total sulfur concentration. The SOLA II contains all apparatus necessary for sample combustion and total sulfur measurement by PUVF.

The SOLA II is an Online Adaptation of the Well-Accepted:

- ASTM D5453 "Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence"
- ISO 20846 "Petroleum Products – Determination of Sulfur Content of Automotive Fuels – Ultraviolet Fluorescence"

Turnkey Sulfur Analyzer System

The SOLA II biofuel analyzer is offered as a turnkey system and includes a stainless steel, climate controlled cabinet complete with all sample conditioning components. The cabinet arrangement is suitable for installation where the expected ambient temperature is within -15°C to +50°C (+5°F to +122°F). In colder climates, a climate controlled, walk-in shelter is recommended. Alternatively, the SOLA II field analyzer system can be rack mounted for installation in an existing test room or shelter *(see figure 3)*. The turnkey system can be configured to provide all equipment necessary for online and at-line sulfur analyses. The user only provides a concrete mounting pad, compressed air at 80 psig and electrical power. Unique features include the cell phone link for remote diagnostics and low utility requirements (cylinder gases are not required).

Unique features of the SOLA II field sulfur analyzer system are:

- At-line capability for grab sample analyses by non-laboratory personnel
- Rapid initial response time (<60 seconds) for online mode
- Automated wireless diagnostics to ensure maximum on-stream time.

Online Sulfur Analysis with the SOLA II

When operating in the online mode, the SOLA II automatically samples the process 24 hours a day, 7 days a week. The SOLA II field analyzer provides initial response to changes in sulfur concentration in 60 seconds or less. The turnkey SOLA II field analyzer system comes complete with all sample conditioning accessories necessary for sample transport and filtration. Sulfur data may be communicated to your control system by traditional 4-20 mA signals and/or Modbus. Correction of ppm S (w/w) for changes in product gravity is accomplished by a fixed constant or a 4-20 mA input from a field gravitometer. The gravitometer can be supplied as part of the turnkey SOLA II field sulfur analyzer system.

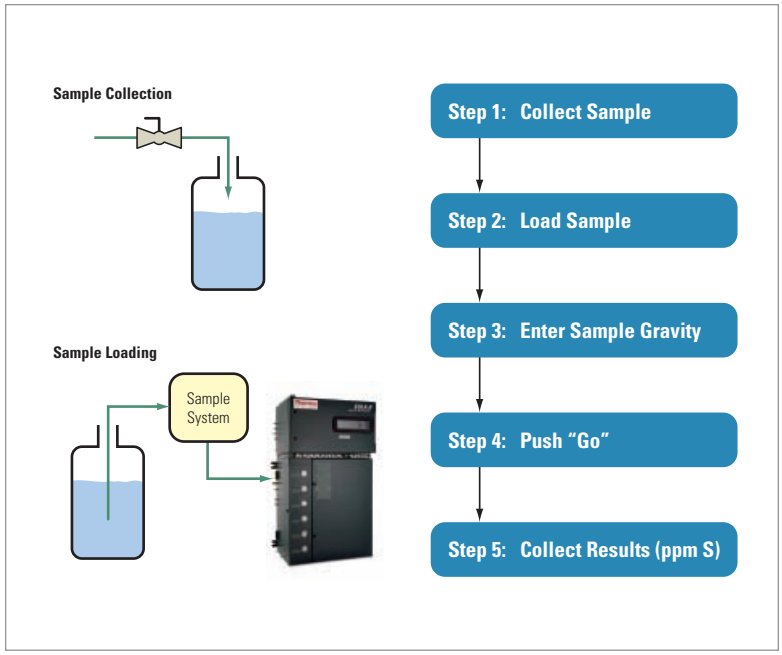

figure 4 – At-line sulfur analysis with the SOLA II

Maintenance

Thermo Fisher Scientific offers several levels of maintenance contracts to ensure the SOLA II field sulfur analyzer delivers maximum on-stream time. Should you select our all inclusive maintenance contract, Thermo Fisher takes care of all SOLA II maintenance and spare part needs. Under the all inclusive maintenance contract, we will make four preventative maintenance visits per year. Between preventative maintenance visits, Thermo Fisher will monitor your SOLA II with our proven AutoSCAN® system. AutoSCAN automatically polls the SOLA II via a cell phone link, 24 hours/day, 7 days/week. Thermo Fisher's service staff utilizes AutoSCAN to plan preventative visits and respond to fault conditions. Our service engineers review AutoSCAN reports of system operating parameters prior to dispatch to ensure effective preventative maintenance visits. Should AutoSCAN detect a fault condition, Thermo Fisher's service department is automatically notified and a service engineer is dispatched.

Summary

- The SOLA II field sulfur analyzer system rapidly determines sulfur content in biofuels.
- The SOLA II provides biofuel manufacturers with a single, turnkey system for all grab sample and online sulfur measurement needs.
- The SOLA II's reliable online analysis ensures shippers consistently deliver ultra low sulfur biofuels at the targeted sulfur specification.
- All inclusive maintenance contracts, in combination with the unique SOLA II / AutoSCAN integrated analyzer maintenance system, enable users to keep the SOLA II in top operating condition.

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Specifications

Field Enclosure	
Material of Construction	304 SS
Dimensions (not including sun shade)	78 in W x 60 in H X 24 in D (selected options may alter final dimensions)
Ambient Temperature Limits	-15°C to +50°C (+5°F to +122°F)
Hazardous Area Classification	NEC Class 1, Div. 1, Groups B, C, D or NEC Class 1, Div. 2, Groups B, C, D CSA with associated "C/US Mark" Class 1, Div. 1, Groups B, C, D or Class 1, Div. 2, Groups B, C, D ATEX Zone 1, EEx p IIC T2 (T3, T4 optional) or Zone 2, EEx p IIC T2 (T3, T4 optional) CE Mark For other classifications consult factory
Disconnect Switches	One for each 120 VAC circuit
Junction Boxes	Separate signal and 120 VAC junction boxes
Utility Requirements	
Compressed Air	8 SCFM @ 80 psig, minimum (air clean-up system included)
Electrical Power	120 VAC (selected options will determine number of circuits and wattages)
SOLA II Field Sulfur Analyzer	*(see SOLA II data sheet for complete specifications)*
Method of Analysis	Pulsed Ultraviolet Fluorescence, PUVF
Data Communications (Outputs)	RS 485 Modbus and/or 4-20 mA analogs
Required Inputs	A 4-20 mA input from a densitometer (gravitometer) is required for density compensation
Sampling Frequency	Two injections per minute
Initial Response Time	60 seconds or less, not including sample transport time
Optional Densitometer	*(see Thermo's Sarasota FD 910 data sheet for complete specification)*
Model	Sarasota FD910
Principle of Operation	Vibrating Tube
Power Supply	Powered by SOLA II
Sample Conditioning System	
Fast Loop	Sized to minimize sample transport time, includes: isolation valves, flow control/indication and filtration
Optional Fast Loop Sample Pump	Class 1, Division 2, Group C,D; 120 VAC: self priming, sized per site requirements
Slipstream	Delivers sample from fast loop to SOLA II, includes: isolation valves, flow control/indication, secondary filtration, sample flow switch and high/low flow select valve to minimize consumption of validation and/or calibration fluids
Stream Selection	Automatic pneumatically operated valves to select online or at-line analysis mode (optional)
At-Line Analysis Option	Includes dedicated self priming Class 1, Division 2, Group C,D pump for introduction of grab samples (pressurization of sample containers not required) all required flow control apparatus and pneumatically operated sample select valves
Validation/Calibration Sample Selection	Requires optional at-line analysis mode or pressurized validation/calibration tank
Validation/Calibration Tank	20 liters (5.3 gal) included with at-line analysis option

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